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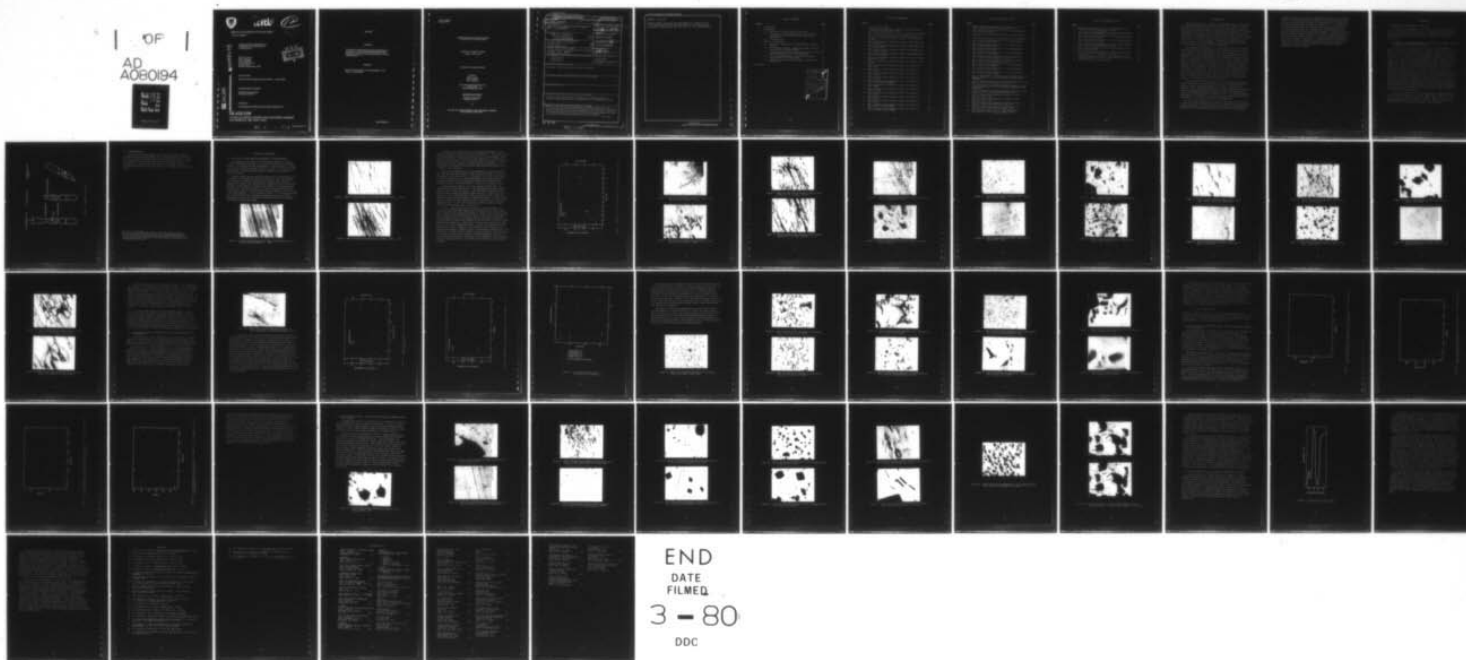
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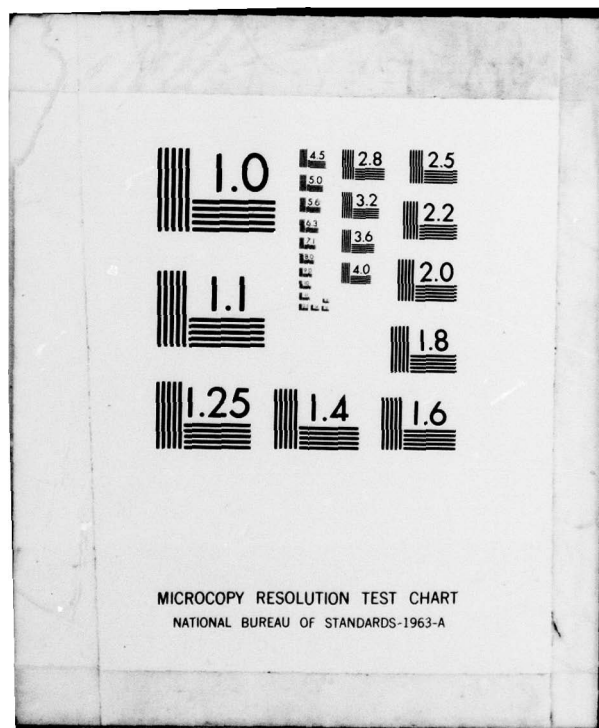
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Research and Development Technical Report

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INVESTIGATION OF METHODS TO ELIMINATE VOLTAGE DELAY IN Li/SOCl₂ CELLS

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Quarterly Technical Report for Period 19 March - 19 June 1979

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QUARTERLY TECHNICAL REPORT
19 March - 19 June 1979

CONTRACT NO. DAAB07-78-C-0558

Prepared by
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ABSTRACT - Continued

↙ Micropolarization and capacitance measurements of lithium stored in 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{16}/\text{SOCl}_2$ have indicated that the film formed in this electrolyte is much thinner than that formed in 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$. ↘

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1. INTRODUCTION

This report is part of a continuing fundamental study of the formation and growth of lithium chloride films on lithium metal exposed to thionyl chloride electrolytes, and how the electrolyte salts LiAlCl_4 , $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$, and $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$ affect both the film growth and the voltage delay or startup characteristic of primary cells following storage at ambient or elevated temperature. The thickness of the lithium chloride film on lithium in these cells has been correlated with the severity of the voltage delay following storage (1-5). The salt $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ was reported to alleviate voltage delay when used in place of LiAlCl_4 , although the mechanism responsible for this dramatic improvement was not established.

The thickness and resistivity of films on active metals in corrosive electrolytes have been measured using a galvanostatic pulse technique and by the weight gain of lithium samples stored with electrolytes in glass ampoules (6-10). These studies have led to the development of the solid electrolyte interphase (SEI) model for these systems. According to this theory, contact between lithium and solutions containing thionyl chloride causes the formation of a thin insoluble film of lithium chloride which completely covers the metal, preventing further rapid chemical attack by stopping solvent transport, but allowing anodic discharge by permitting the passage of lithium ions. The measurements seem to indicate that the film consists of two layers. The first, a thin compact layer next to the metal and referred to as the SEI, is said to be overlain with a porous and much thicker layer of lithium chloride crystals. The outer layer is thought to be responsible for the voltage delay (10).

During the present quarter, weight gain and scanning electron microscopic examination of lithium stored in various electrolytes were to be compared, using 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ as the control electrolyte (10). Micropolarization measurements performed on lithium samples stored in cells containing $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$ were planned to compare with controls containing $\text{LiAlCl}_4/\text{SOCl}_2$, previously studied (11, 12). The micropolarization measurements are non-destructive, and cells may be stored again following measurements of the surface resistivity and capacitance.

The two general objectives of this work continue to be to establish to what extent the polyhedral borate salts are more effective than lithium tetrachloroaluminate in preventing heavy film formation, electrochemical passivation, and voltage delay, and to establish by what mechanisms the

polyhedral borate salts are able to accomplish their effect. An adequate solution to the delay problem would require that neither extensive anode corrosion, self-discharge, or other cell deterioration is a consequence of any changes made in the electrolyte composition. If the borate salts prove to be substantially more effective than LiAlCl_4 as electrolytes in Li/SOCl_2 power sources, an understanding of the mechanism by which this occurs may make alternative solutions possible. Alternative solutions would be desirable because synthesis of the borate requires expensive, reactive, and toxic starting materials, and because adequate purification of the final products is difficult. A continued study of the physical properties of lithium polyhedral borates/thionyl chloride solutions was therefore planned to include the analysis of visible and electron paramagnetic resonance spectra.

2. EXPERIMENTAL

2.1 MATERIALS AND ELECTROCHEMICAL TEST CELLS

The synthesis of $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$, the purification of thionyl chloride, and the preparation of 0.25 M solutions of $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ in thionyl chloride, have all been previously described (11-12). Electrochemical test cells for pulse polarization measurements were also prepared as described previously (13).

2.2 PREPARATION OF GLASS AMPOULES USED IN THE ANALYSIS OF LITHIUM CORROSION BY WEIGHT GAIN AND BY SEM OBSERVATION.

The ampoules used to measure the weight gain of lithium samples exposed to solvents and electrolytes and to examine lithium samples in the SEM were prepared in the following way. Pieces of lithium foil 2 cm x 6 cm were rolled up with sections of 5 mil thick Crane non-woven glass fabric and inserted in glass tubes such as diagrammed in Figure 1a after exactly 10 ml of the fluid to be tested had already been added to the tube. The tubes were attached to a vacuum line, frozen in liquid nitrogen, and then pumped down. The liquid was permitted to thaw in order to allow any trapped gas to escape, and the tube was once again frozen and evacuated. The tube was then sealed off with a torch as indicated in Figure 1b, inverted as indicated in Figure 1c, and stored at the appropriate temperature for the appropriate period of time. When it came time to examine the stored lithium, the ampoules were taken into an argon filled dry box and broken open where indicated by the arrow in Figure 1b. Each lithium roll was either carefully unravelled, washed twice with thionyl chloride and weighed after being allowed to dry, or a small piece was sectioned off, washed and mounted for examination under the scanning electron microscope. The samples were transferred to the microscope with the aid of sealed jars and a nitrogen filled antechamber.

In all these experiments the ratio of the area of exposed lithium to the electrolyte volume (A/V) was $2.4 \text{ cm}^{-1} \left(\frac{24}{10}\right)$ which is near that in the AA cells used for startup and capacity studies. $\left(\frac{13}{4} = 3.25 \text{ cm}^{-1}\right)$. The stored lithium was not in contact with any other metal, eliminating the possibility of self discharge through local cell reactions.

1A - TUBE BEFORE SEAL OFF

1B - TUBE AFTER SEAL OFF

1C - TUBE INVERTED FOR STORAGE

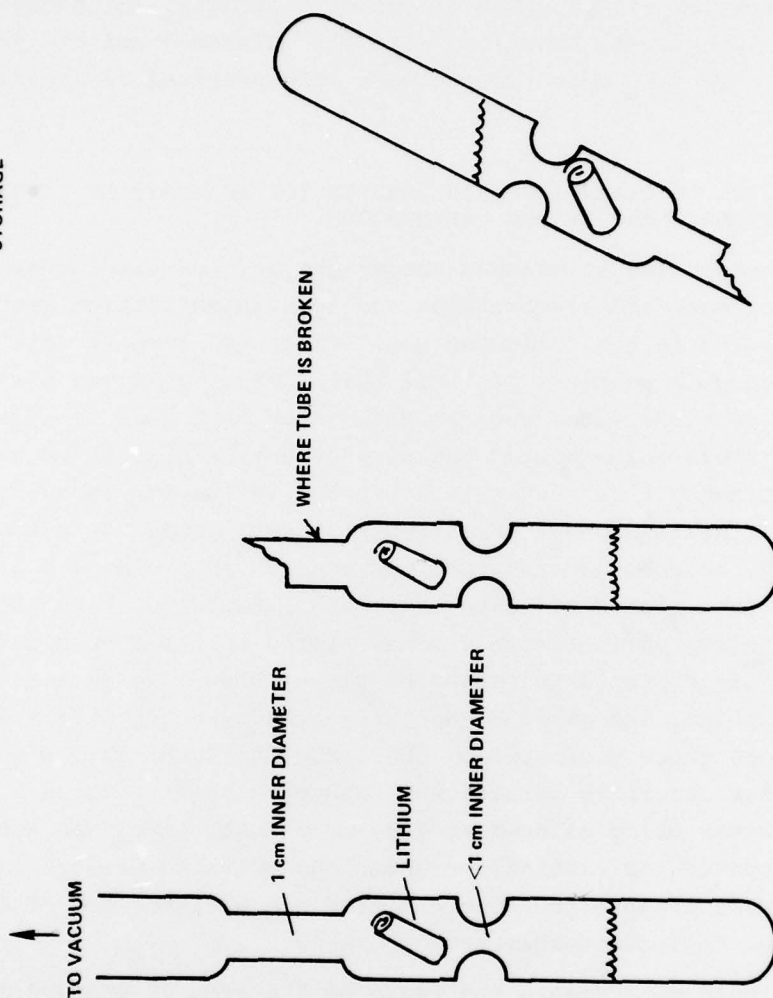


Figure 1. Sealed Corrosion Tube

2.3 INSTRUMENTATION*

Scanning electron micrographs were taken using a JSM-U3 scanning electron microscope manufactured by JEOL. X-ray dispersion analysis was carried out using a Princeton Gamma Tech PGT-1000 X-Ray analyser. It was not calibrated. Visible spectra were taken with reference to air in a 5 mm quartz cell using a Cary 14 recording spectrometer. Electron paramagnetic resonance spectra were taken on an instrument manufactured by Varian.

* We wish to acknowledge with thanks the SEM photographs prepared by Mr. Kim Ostreicher, GTE Laboratories, the visible spectra prepared by Mr. Frank Kochanek and Mr. Paul Martakos, also of GTE Laboratories, and the EPR spectra, taken by Dr. Hans van Willigen of the University of Massachusetts, Boston.

3. RESULTS AND DISCUSSION

3.1 PURE SOCl_2 : WEIGHT GAIN AND SEM STUDIES OF LITHIUM SAMPLES

To establish the validity of our experimental approach, scanning electron micrographs were taken of an untreated lithium surface (Figures 2 and 3) as it arrived from the manufacturer. Figure 4 shows the lithium surface after momentary exposure to thionyl chloride. It can be seen that the procedure of washing the SEM samples in thionyl chloride did not produce artifacts.

From the weight gain per square centimeter, the film thickness can be calculated if the composition of the film is known. The film thickness and the depth to which the lithium was corroded have been calculated assuming all lithium which reacted formed an adhering film of pure lithium chloride. These numbers (in microns) are entered in all figures showing weight gains. The slight solubility of LiCl may have caused attrition, or dissolution from the film and crystallization elsewhere, as on the sides of the glass ampoules. If any attrition occurred, or if the coating was not pure lithium chloride, the calculated thicknesses have been affected. Nonetheless, they provide a valuable estimate of average film thickness on the chemically passivated sample.

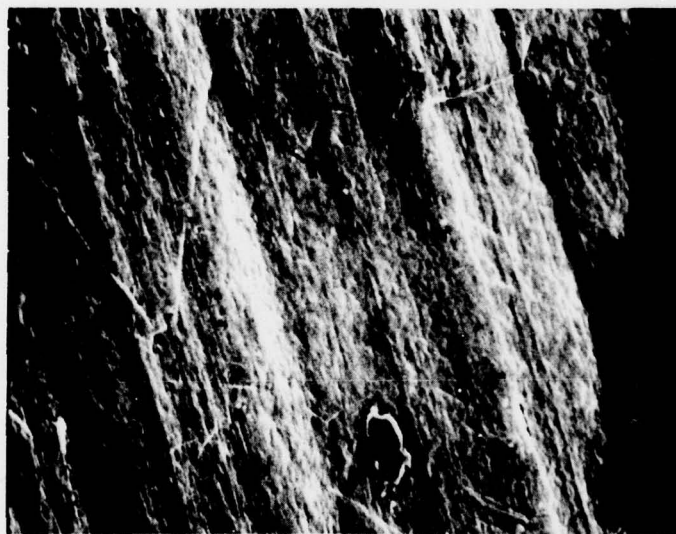


Figure 2. Scanning Electron Micrograph (SEM) of Lithium Surface as it Arrives from Manufacturer X300

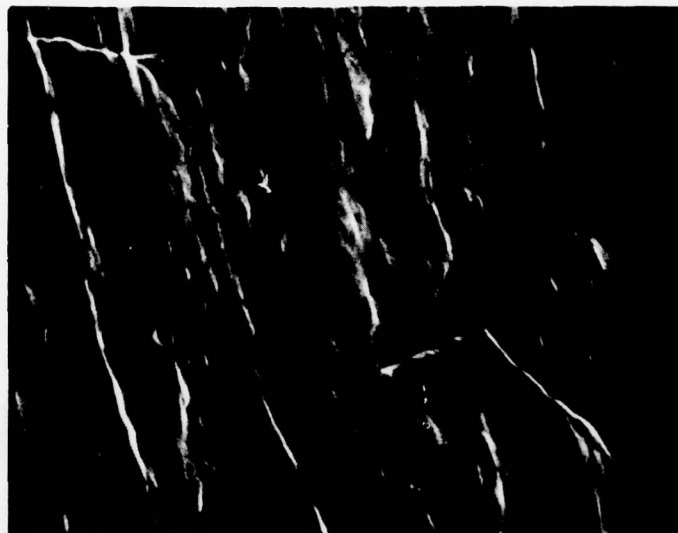


Figure 3. SEM of Lithium Surface as it arrives from Manufacturer X3000

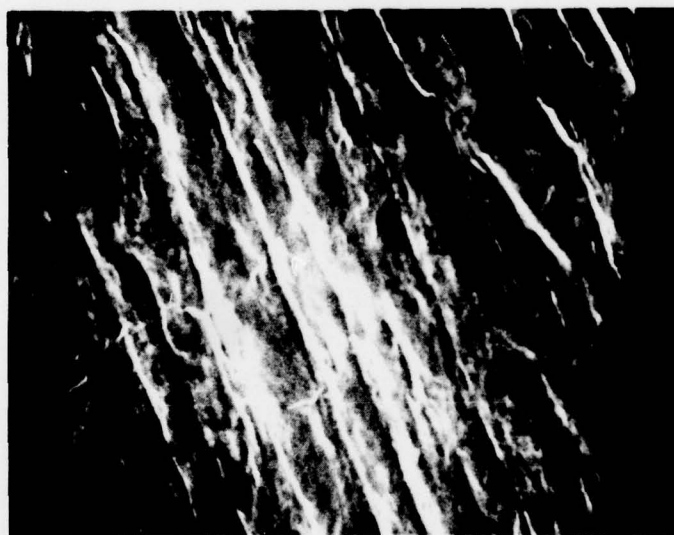


Figure 4. SEM of Lithium Surface Momentarily Exposed to SOCl_2 X300

In Figure 5, the weight gains of lithium samples immersed in pure SOCl_2 are plotted as a function of time and temperature. The weight gain in these experiments was small and the uncertainty in the measurement caused scatter in the data. On the basis of these experiments, the storage temperature did not appear to have affected the extent of corrosion. However, the weight gained as a result of lithium corrosion and growth of LiCl on the surface of the metal may have fortuitously balanced the weight lost as a result of LiCl attrition.

When lithium samples stored at room temperature in thionyl chloride were examined under the scanning electron microscope (SEM), no crystals were observed (see Figures 6-10). In Figures 6, 7, and 10, the corrosion of lithium appeared to be a localized phenomenon under these conditions. As shown in Figures 8 and 9, the surface became very roughened after extended storage at room temperature but there were no obvious crystals.

Lithium samples stored at 55° in pure thionyl chloride were also examined after 25 and after 80 days. The development of surface features after 25 days is shown in Figure 11. After 80 days of such storage the surface of the lithium had roughly shaped crystals on it as can be seen in Figures 12 and 13, which were both taken on the same sample. While the surfaces in these two photographs are somewhat different, the basic similarities can be seen at higher magnification in Figures 14 and 15 of the same respective areas. A side view of the rough, almost crystalline surface stored for 80 days can be seen in Figure 16.

At 72°C , lithium stored with pure thionyl chloride acquired a more crystalline appearance when compared with lithium stored at lower temperature. Figures 17 and 18 show the surface of a sample after 25 days storage. Again the beginning of crystalline development can be seen. Photographs at the same magnification of a surface at the same temperature for 83 days reveal extensive crystallinity (Figures 19 and 20) which is visible at lower magnification (Figure 21). Side views of the crystals revealing how rough they are, are seen in Figures 22 and 23. Crystals are normally formed by growth from solution. Exchange of solid material with the solution will encourage the growth of larger crystals at the expense of smaller ones, since the surface to volume ratio is larger for smaller crystals. The solubility of a compound and the rate at which solid may exchange with material in solution are usually greater, the higher is the temperature. The conclusion is that lithium chloride has a small but finite solubility in pure thionyl chloride.

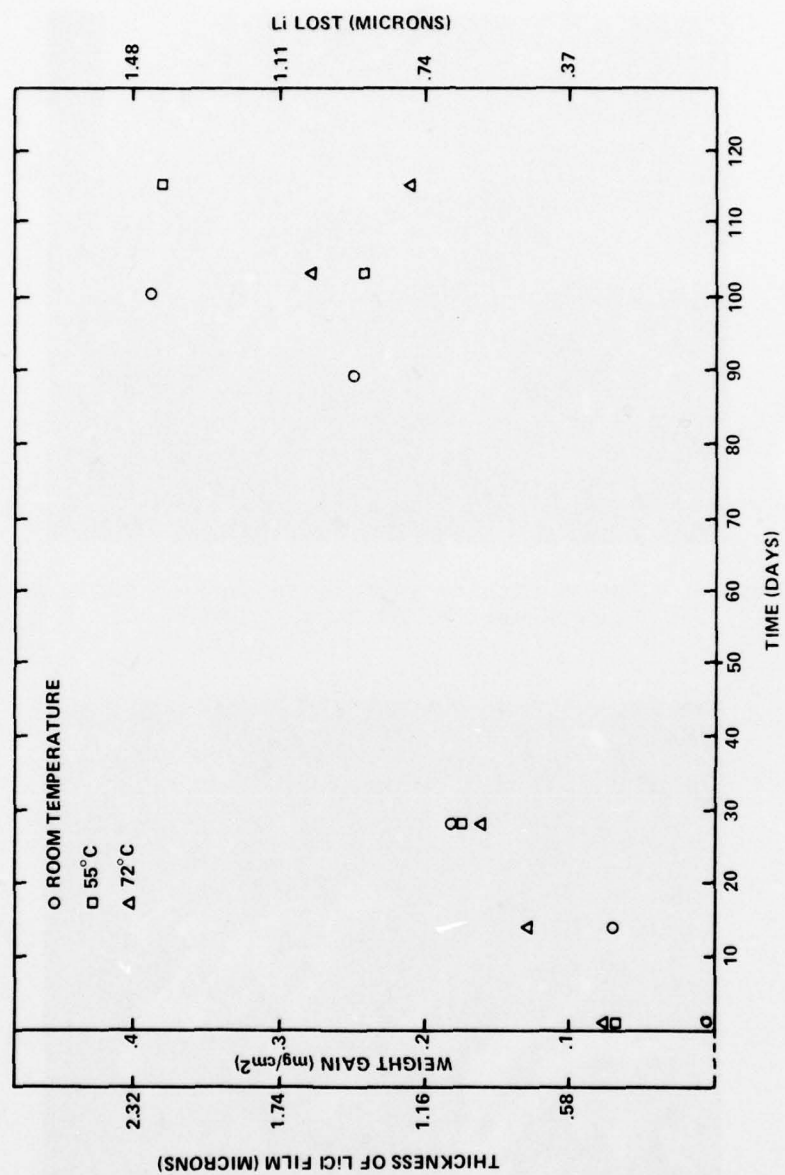


Figure 5. Weight Gain for Lithium Samples Stored in Sealed Ampoules of SOCl_2



Figure 6. SEM of Lithium Surface Exposed to SOCl_2 at Room Temperature for 59 Days. X100

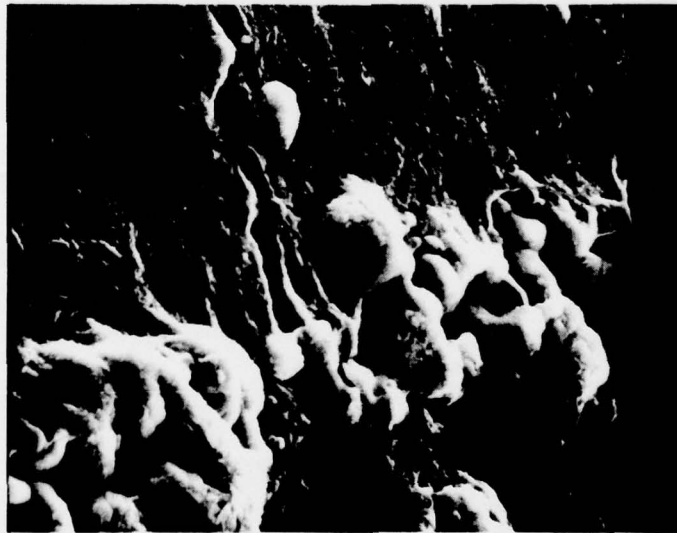


Figure 7. SEM of Lithium Surface Exposed to SOCl_2 at Room Temperature for 59 Days. X1000

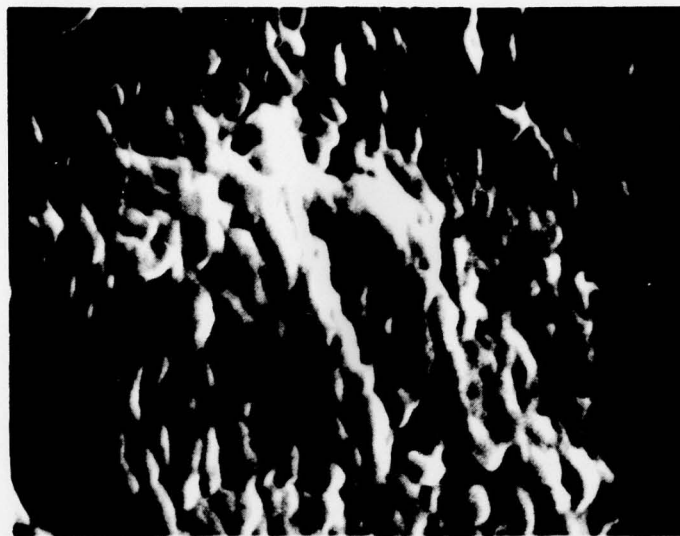


Figure 8. SEM of Lithium Surface Exposed to SOCl_2 at Room Temperature for 59 Days. X10,000

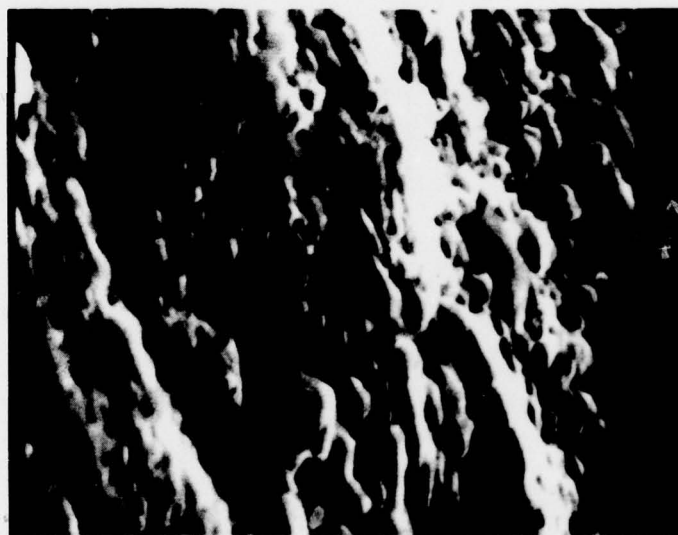


Figure 9. SEM of Lithium Surface Exposed to SOCl_2 at Room Temperature for 59 Days. X10,000

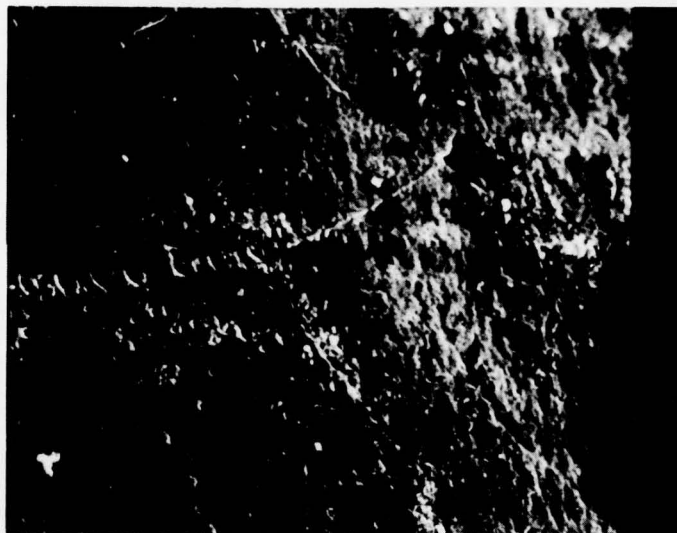


Figure 10. SEM of Lithium Surface Exposed to SOCl_2 for 25 Days at Room Temperature. . X300

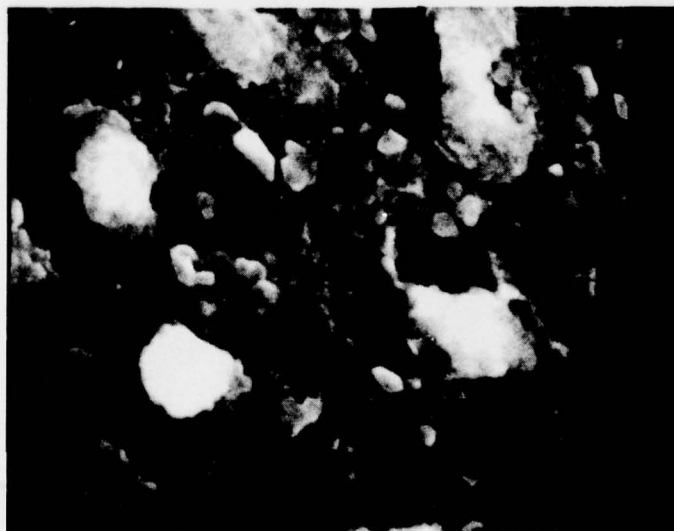


Figure 11. SEM of Lithium Surface Exposed to SOCl_2 for 25 Days at 55°C. X10,000

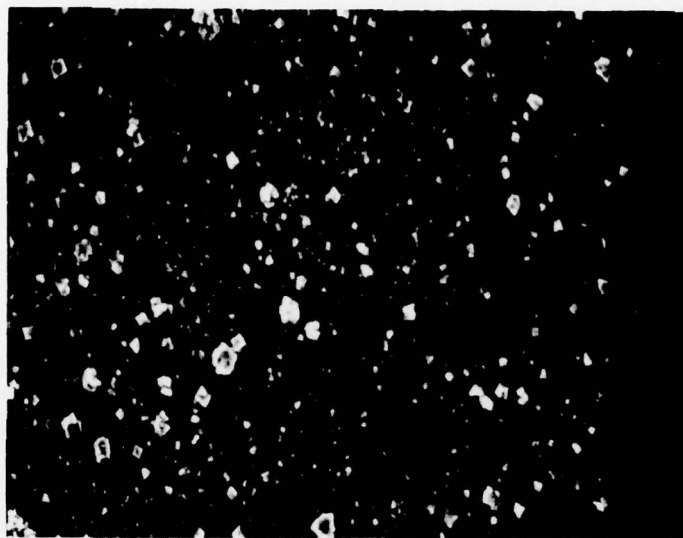


Figure 12. SEM of Lithium Surface Exposed to SOCl_2 for 80 Days at 55°C . X300

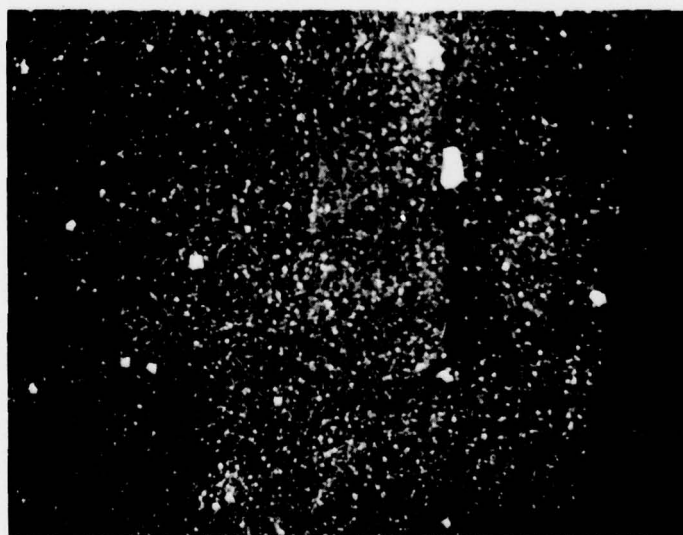


Figure 13. SEM of Lithium Surface Exposed to SOCl_2 for 80 Days at 55°C . X300



Figure 14. SEM of Lithium Surface Exposed to SOCl_2 for 80 Days at 55°C . X3,000

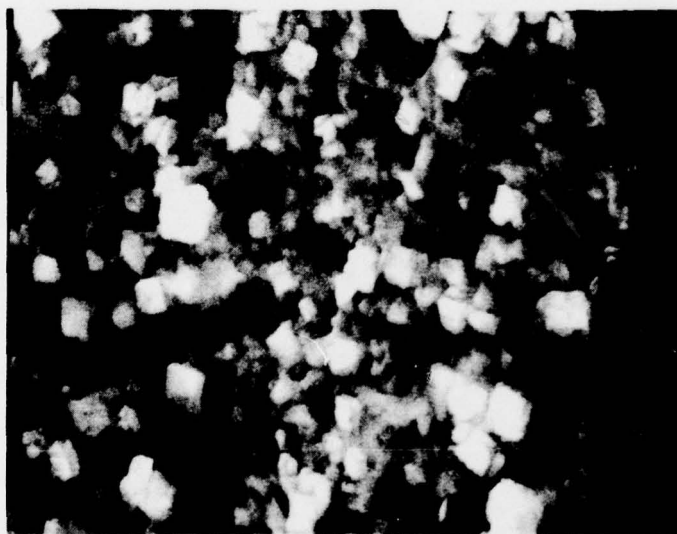


Figure 15. SEM of Lithium Surface Exposed to SOCl_2 for 80 Days at 55°C . X3,000



Figure 16. SEM of Lithium Surface Exposed to SOCl_2 for 80 Days at 55°C . X3000, 85° from Normal.²



Figure 17. SEM of Lithium Surface Exposed to SOCl_2 for 25 Days at 72° , X1000

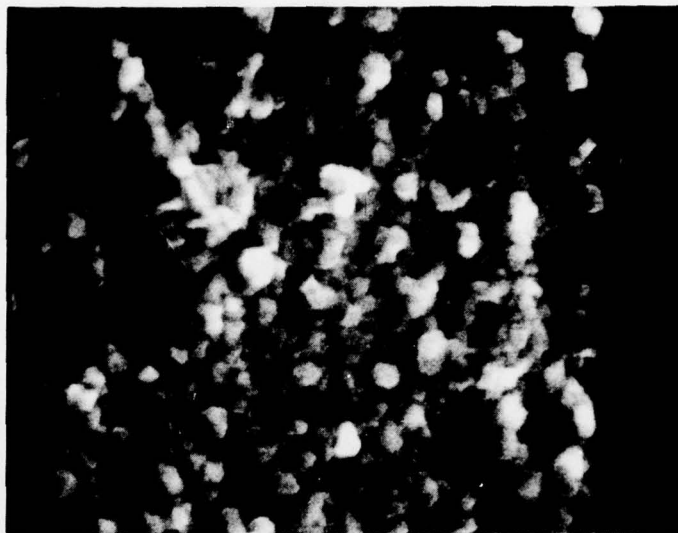


Figure 18. SEM of Lithium Surface Exposed to SOCl_2 for 25 Days at 72°C , X10,000.

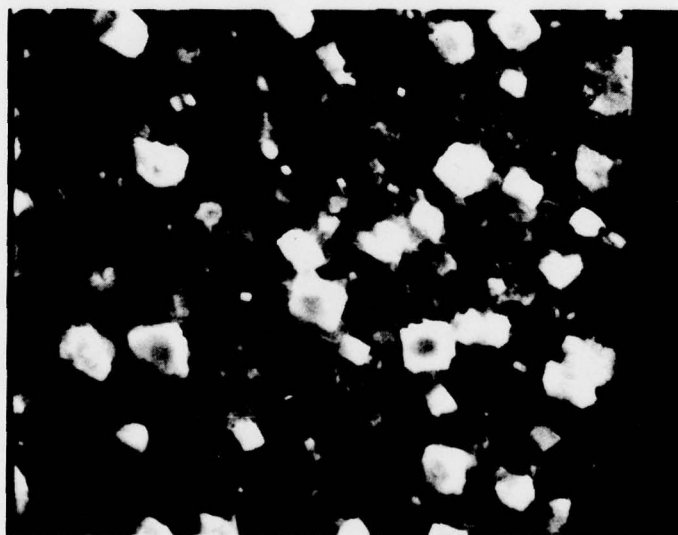


Figure 19. SEM of Lithium Surface Exposed to SOCl_2 for 83 Days at 72°C , X1000.



Figure 20. SEM of Lithium Surface Exposed to SOCl_2 for 83 Days at 72°C , X3000.

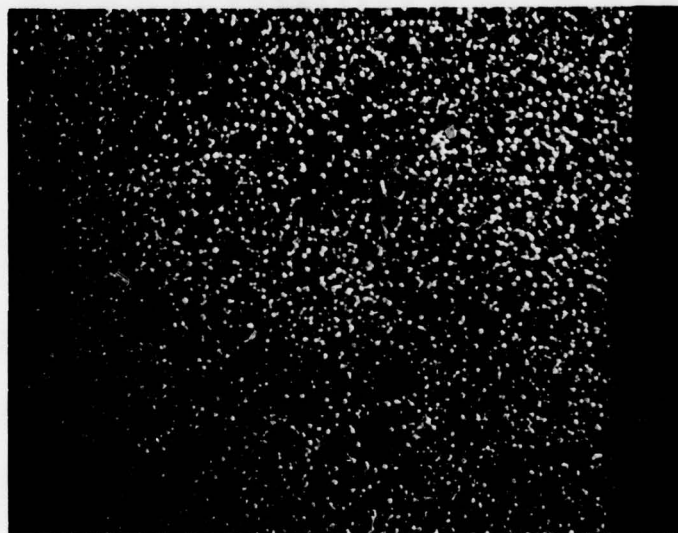


Figure 21. SEM of Lithium Surface Exposed to SOCl_2 for 83 Days at 72°C , X100.

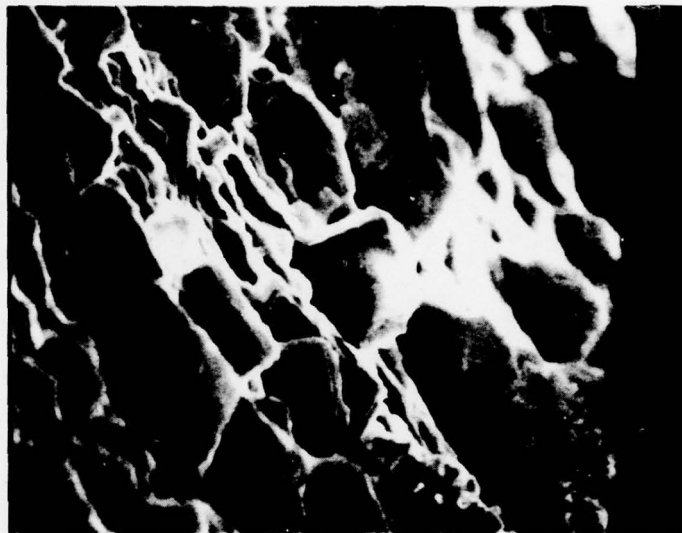


Figure 22. SEM of Lithium Surface Exposed to SOCl_2 for 83 Days at 72°C , X3000; 85° from Normal.²

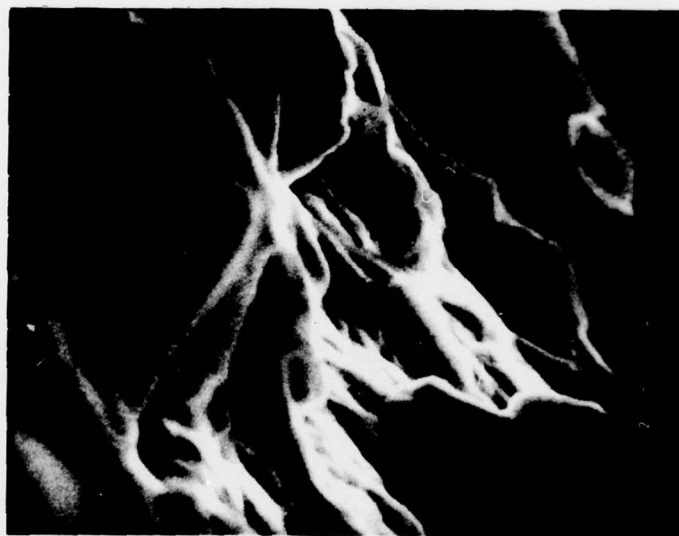


Figure 23. SEM of Lithium Surface Exposed to SOCl_2 for 83 Days at 72° , X10,000; 85° from Normal.²

Lithium metal samples stored in thionyl chloride at room temperature for 50 days at 72°C for 83 days were analyzed by EDAX, or x-ray dispersion, which can detect elements heavier than sodium in specific areas of fields observed with the SEM. In the sample stored at room temperature (see Figure 6), chloride and some sulfur were detected in the smooth areas. The ratio of the peak heights was consistent over the smooth areas. In the localized areas of corrosion, as seen in Figure 7, peak heights were inconsistent, but usually contained more sulfur. EDAX analysis of the crystals on the surface of the lithium stored at 72°C for 83 days (Figure 19) revealed only chlorine. The substrate between these crystals contained sulfur.

In the past, EDAX analysis of lithium surfaces exposed to thionyl chloride have never considered what happens during exposure to the pure solvent, but have always dealt with thionyl chloride containing lithium tetrachloraluminate. Sulfur has never been found in the films on lithium stored with $\text{LiAlCl}_4/\text{SOCl}_2$, although chloride has been in abundance. It is possible that the first rapid film forming reactions in $\text{LiAlCl}_4/\text{SOCl}_2$ could be indiscriminate, and the passivating film nearest the lithium metal could contain a mixture of highly reduced species including sulfur compounds.

3.2 1.8 M LiAlCl_4 IN SOCl_2 : WEIGHT GAIN, SEM, AND MICROPOLARIZATION OF LITHIUM SAMPLES

In contrast to the lack of immediate effect of pure SOCl_2 , momentary exposure of lithium metal to 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ and then rinsing with SOCl_2 had a profound effect on the surface morphology. The formerly smooth surface (see Figure 4) has been roughened as can be seen in Figure 24.

The weight gain of lithium samples stored in 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ is plotted as a function of time and temperature of storage in Figure 25. Based on the assumptions already mentioned, the film thickness can be calculated and is indicated in Figure 25. The temperature appeared to have a large influence on the rate and extent film growth on lithium in this electrolyte. The weight gain in electrolyte was greater than in pure thionyl chloride especially at 72°C, as seen in Figure 26. The presence of the electrolyte salt enhances film growth and corrosion.

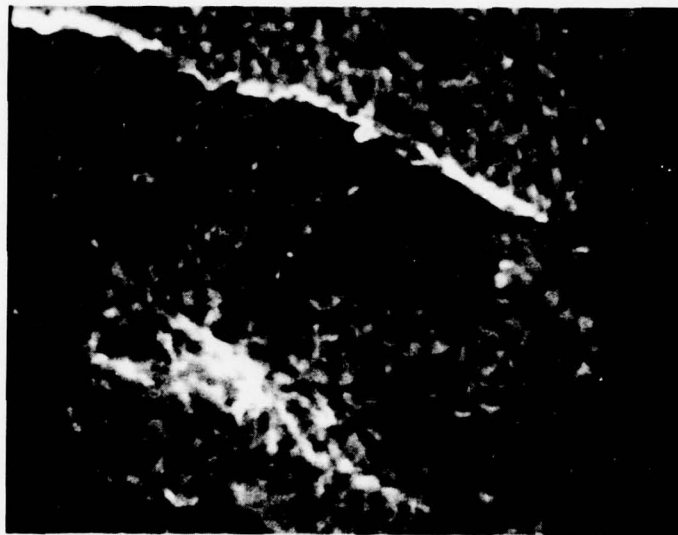


Figure 24. SEM of Lithium Surface Momentarily Exposed to 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ and Rinsed with SOCl_2 ; X10,000

The logarithm of the total film thickness as measured by weight gain and the thickness of the inner layer as calculated from micropolarization measurements are compared as a function of storage time in Figure 27. Calculations based on micropolarization measurements indicated that the average thickness of the SEI was less than 0.5 micron after 30 days at room temperature or at 72°C. The SEM photographs of all lithium samples exposed to 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ showed that the surface structures were greater than 0.5 microns in diameter. Weight gain measurements indicated that the thickness after 30 days was 2.5 microns (room temperature) or about 18 microns (72°C). There are two ways to account for the difference in thickness as determined by the capacitance or by the weight gain measurements. One is the previously proposed theory that there are two films. The other is that there is only one non-uniform passivating layer with deep pores or fissures that go almost all the way through to the metal and whose electrochemical behavior predominates during the micropolarization measurements.

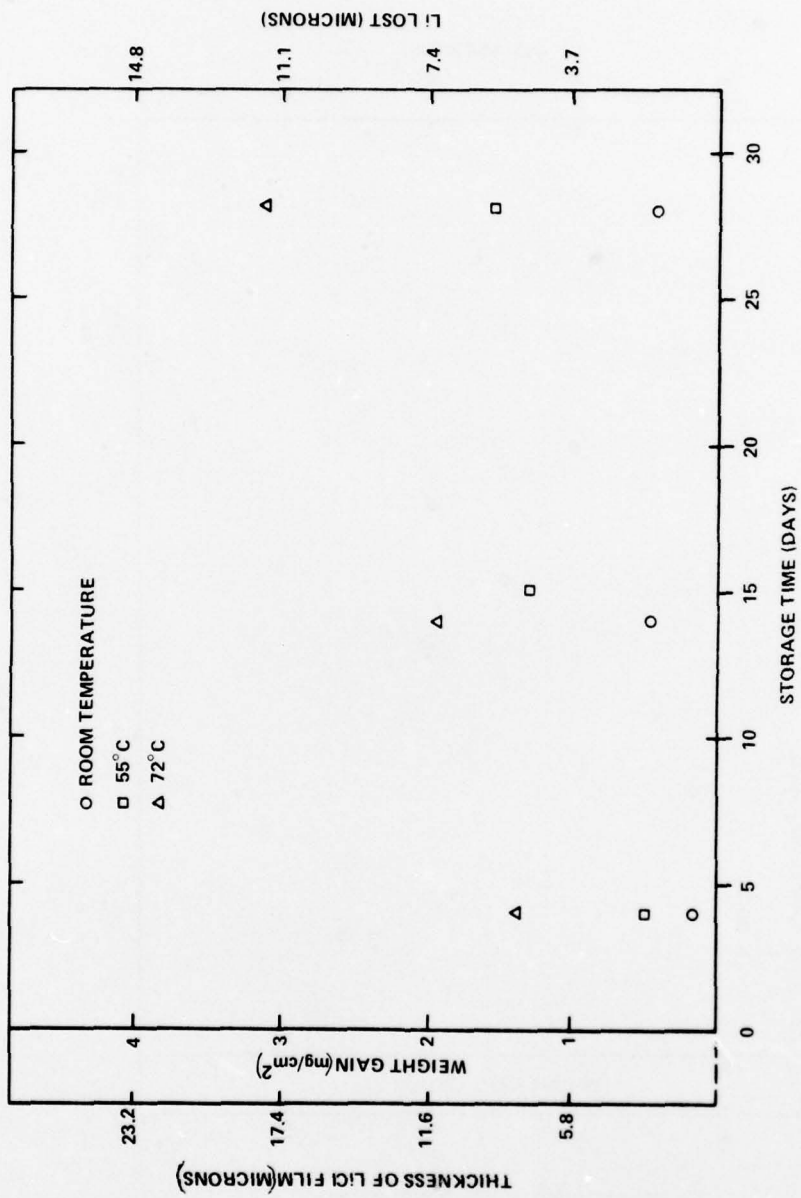


Figure 25. Weight Gain of Lithium Samples Stored in Sealed Ampoules of 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$

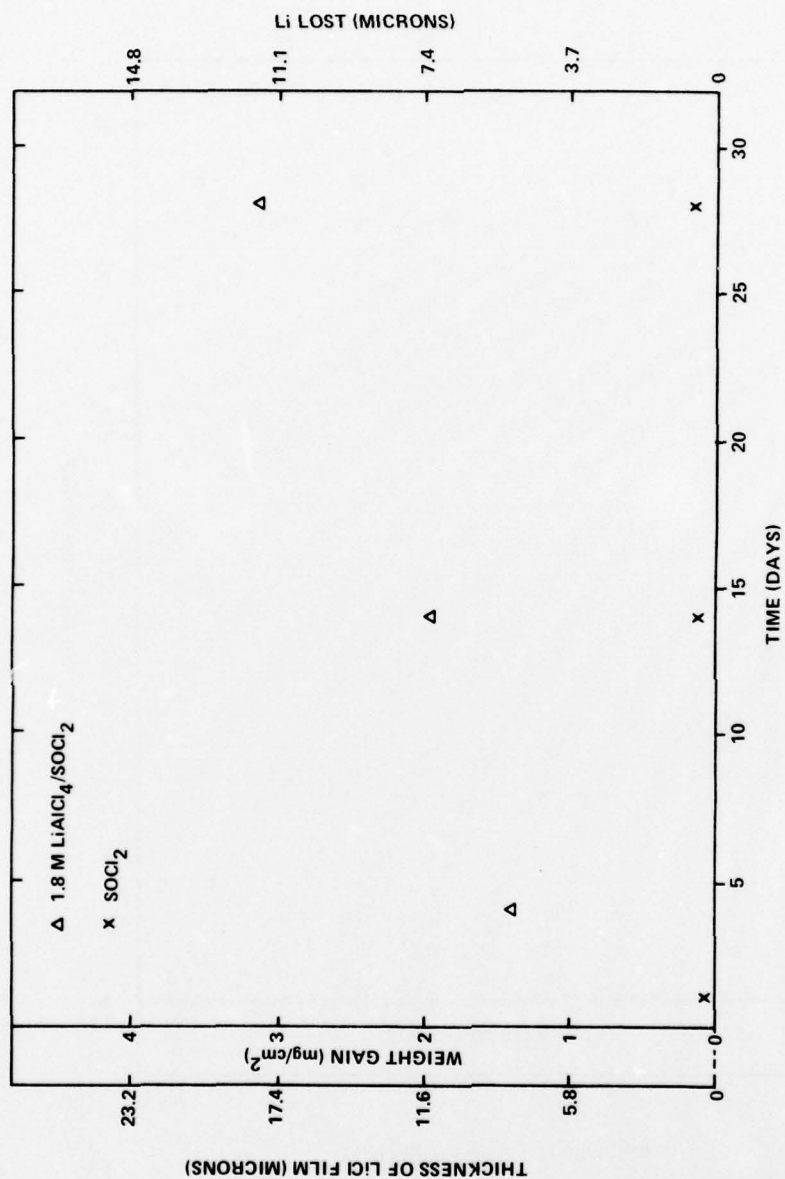
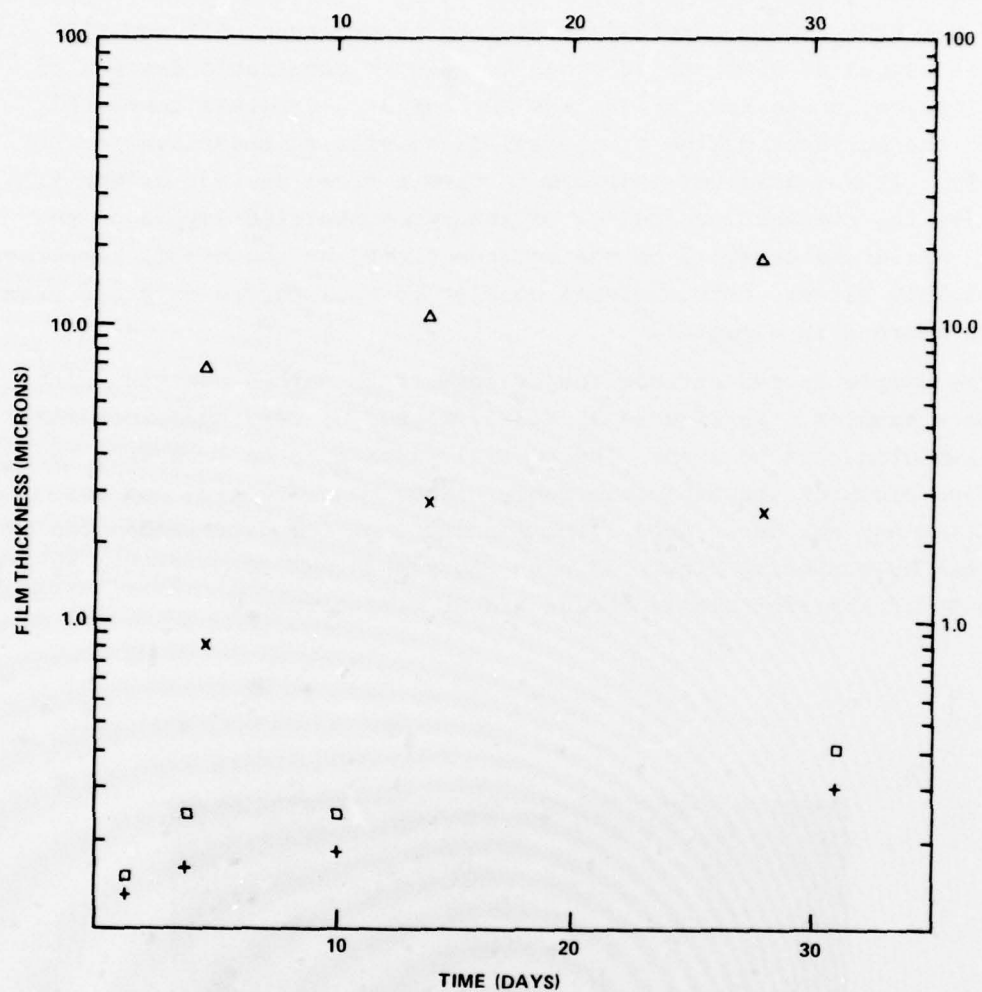


Figure 26. Weight Gain of Lithium Samples Stored in Sealed Ampoules at 72°C



+ CAPACITANCE AT R.T.
 □ CAPACITANCE AT 72°C
 x WEIGHT GAIN AT R.T.
 Δ WEIGHT GAIN AT 72°C
 ALL ON LITHIUM METAL IN 1.8 M LiAlCl₄

Figure 27. Film Thickness Measured by Capacitance and by Weight Gain

Scanning electron micrographs were taken of lithium surfaces stored in 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ for 17 days at room temperature, 55° and 72°C. The surfaces stored at 55°C and 72°C can be seen in comparable degrees of magnification in Figures 28; 29, and 30; and 31. Crystals completely covered the surface, making it impossible to view an underlayer or SEI directly. It was also not possible to view a cross section of the film to verify the presence or absence of the two postulated layers on the metal. While the crystals on the surface stored at the higher temperatures are slightly larger, both surfaces consist of well formed crystals from 3 to 30 microns in diameter.

The sample stored at room temperature is in marked contrast with the above samples. In Figures 32 and 33, a bed of very small crystals under a micron, can be seen. The crystals appear to be less well formed, but these pictures are at considerably higher magnification and the resolution may not be as good. The magnitude of the differences can be seen best by comparing Figure 33 with Figures 34 and 35 or Figure 32 with Figure 36 of the surfaces stored at higher temperature.



Figure 28 - SEM of Lithium Surface Exposed to 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ For 17 Days at 55°C; X300.



Figure 29. SEM of Lithium Surface Exposed to 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ for 17 Days at 55°C; X1000.



Figure 30. SEM of Lithium Surface Exposed to 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ for 17 Days at 72°C; X300.



Figure 31. SEM of Lithium Surface Exposed to 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ For 17 Days at 72°C; X1000.

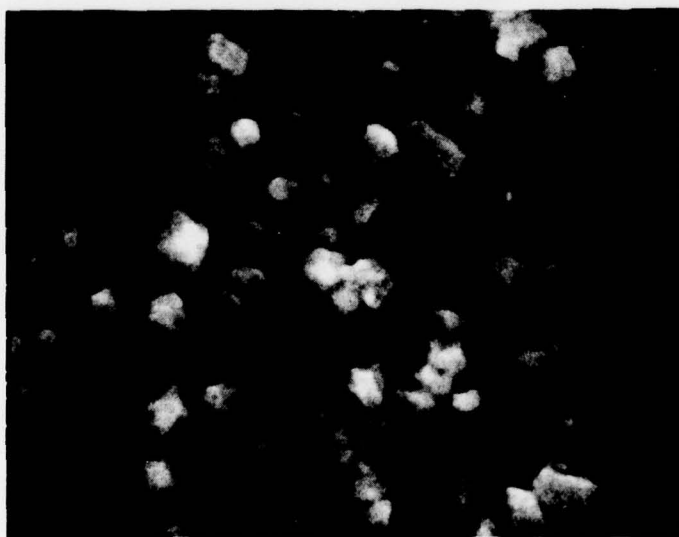


Figure 32. SEM of Lithium Surface Exposed to 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ For 17 Days at Room Temperature; X10,000.

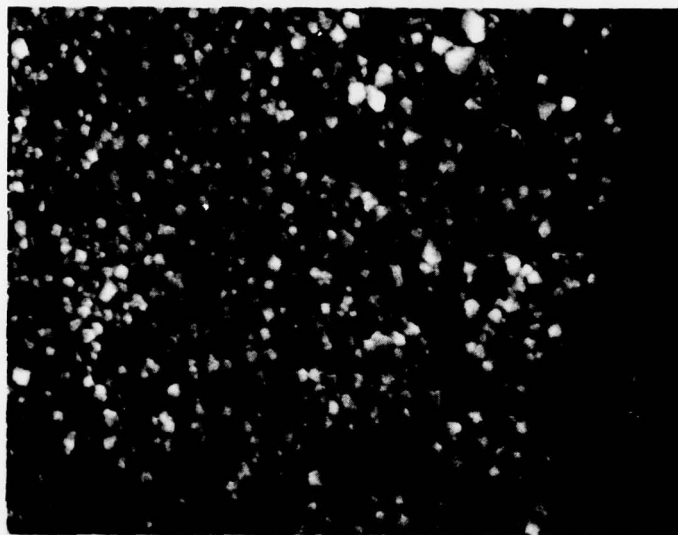


Figure 33. SEM of Lithium Surface Exposed to 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ For 17 Days at Room Temperature; X3000



Figure 34. SEM of Lithium Surface Exposed to 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ For 17 Days at 55°C; X3000.



Figure 35. SEM of Lithium Surface Exposed to 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$
For 17 Days at 72°C; X3000



Figure 36. SEM of Lithium Surface Exposed to 1.3 M $\text{LiAlCl}_4/\text{SOCl}_2$
For 17 Days at 55°C; X10,000.

These results may be compared with growth of LiCl crystals on lithium stored in thionyl chloride alone, as discussed above. The increased temperature of storage, having produced larger crystals on the lithium surface, probably did so by increasing the solubility of lithium chloride in the electrolyte or by causing faster exchange of solid with dissolved salt. The presence of crystals on samples stored at room temperature in $\text{LiAlCl}_4/\text{SOCl}_2$ may indicate that the solubility of LiCl is higher, or the exchange of solid with dissolved salt is faster than in pure thionyl chloride at room temperature. The exchange could occur through reversible dissociation of tetrachloraluminate, as follows:



Increased solubility or exchange of solid lithium chloride with the solution could have caused increased attrition of the film on the lithium, crystallization on the walls of the ampoule, and some systematic error in the measurement of film thickness by weight gain.

3.3 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$: MICROPOLARIZATION OF LITHIUM SAMPLES AND COMPARISON WITH $\text{LiAlCl}_4/\text{SOCl}_2$.

The thickness (d_{\min}) of the chemically passivating film, calculated as described previously (12), is shown as a function of storage time for representative electrodes in 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$ and 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ at room temperature (Figure 37), and at 55° (Figure 38). The thickness of the film on the electrode stored in 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ was less. The film also did not appear to continue growing as fast after the first 3 or 4 days, in contrast to LiAlCl_4 where the film continued to grow for a month or more. The film thickness was found to be more strongly temperature dependent in the boron electrolyte.

The reaction resistance (R_r) of the film on lithium electrodes stored at room temperature in 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$ was two orders of magnitude less than in 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$, as is shown in Figure 39. The reaction resistance of the film found in the boron electrolyte was also more strongly dependent on the storage temperature than it was in the aluminum electrolyte, as shown in Figure 40.

It has been proposed that there are two passivating films on the lithium electrode, an inner one functioning as a solid electrolyte interphase, and an outer one of corrosion products causing the voltage delay (10). It might be expected that if an electrolyte based on $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ alleviated voltage delay (15), the inner film would be more passivating, preventing build-up of the outer film. However, the thickness and

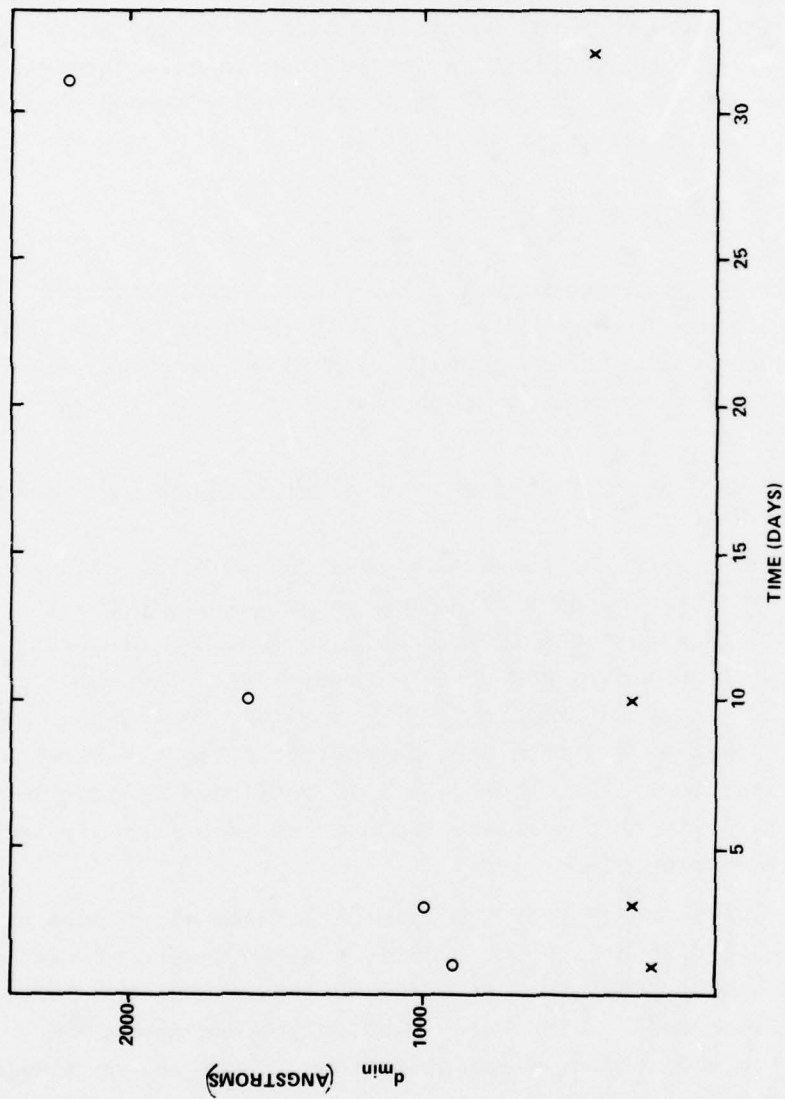


Figure 37. d_{min} For Representative Lithium Electrodes Immersed in .25 M $Li_2B_{10}C_{10}/SOCl_2$ (X) and 1.8 M $LiAlCl_4/SOCl_2$ (O) Stored at Room Temperature.

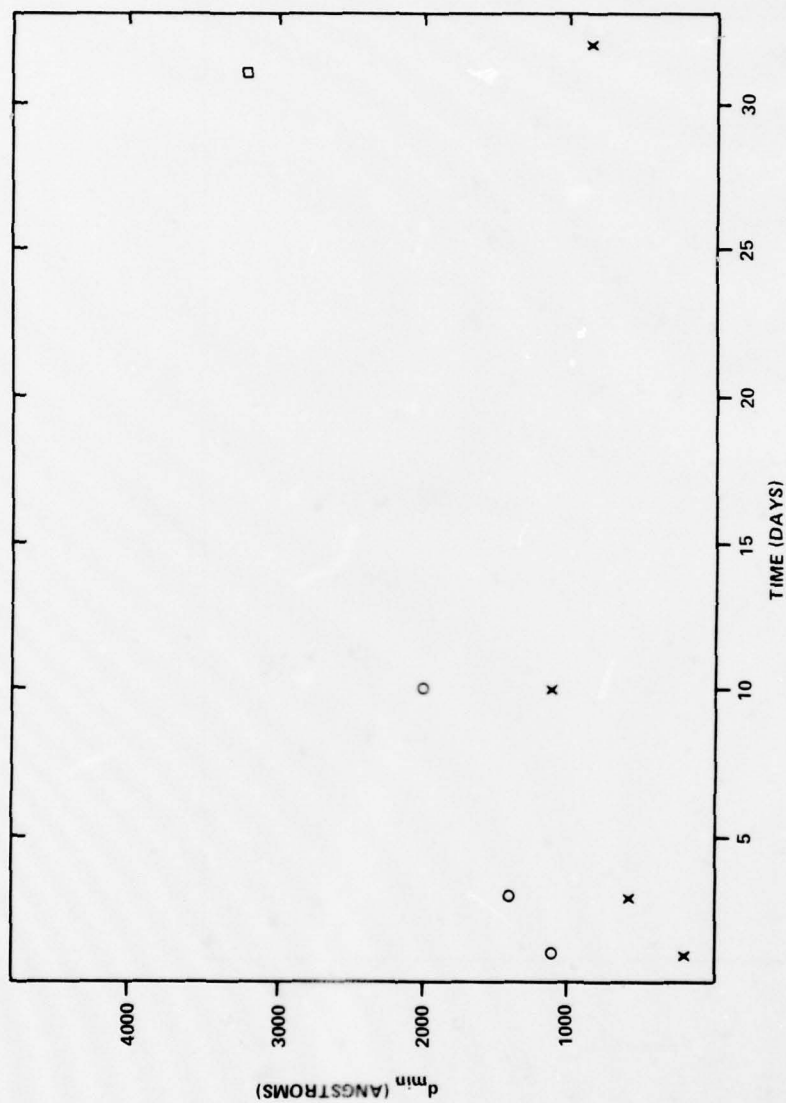


Figure 38. d_{min} For Representative Lithium Electrodes Immersed in $0.25 \text{ M Li}_2\text{B}_{10}\text{Cl}_{10}$ (X) and 1.8 M LiAlCl_4 (O) Stored at 55°C .

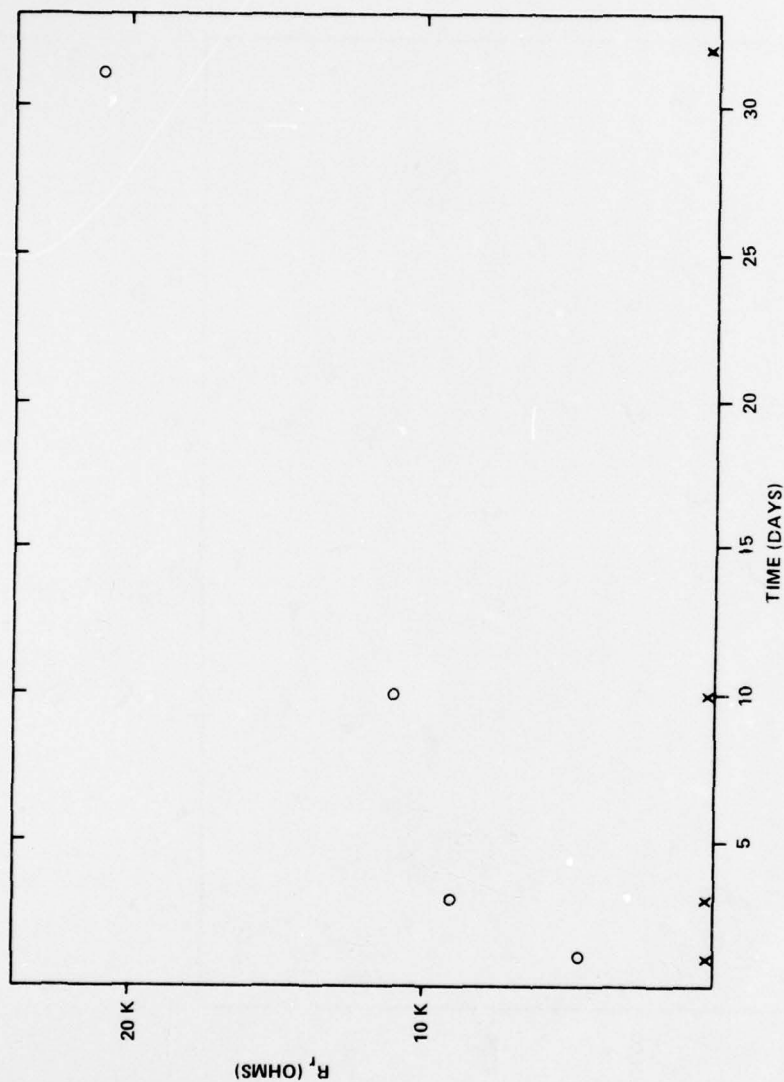


Figure 39. R_p For Representative Lithium Electrodes Immersed in .25 M Li₂B₁₀Cl₁₀/SOCl₂ (X) and 1.8 M Li AlCl₄/SOCl₂ (O) Stored at Room Temperature.

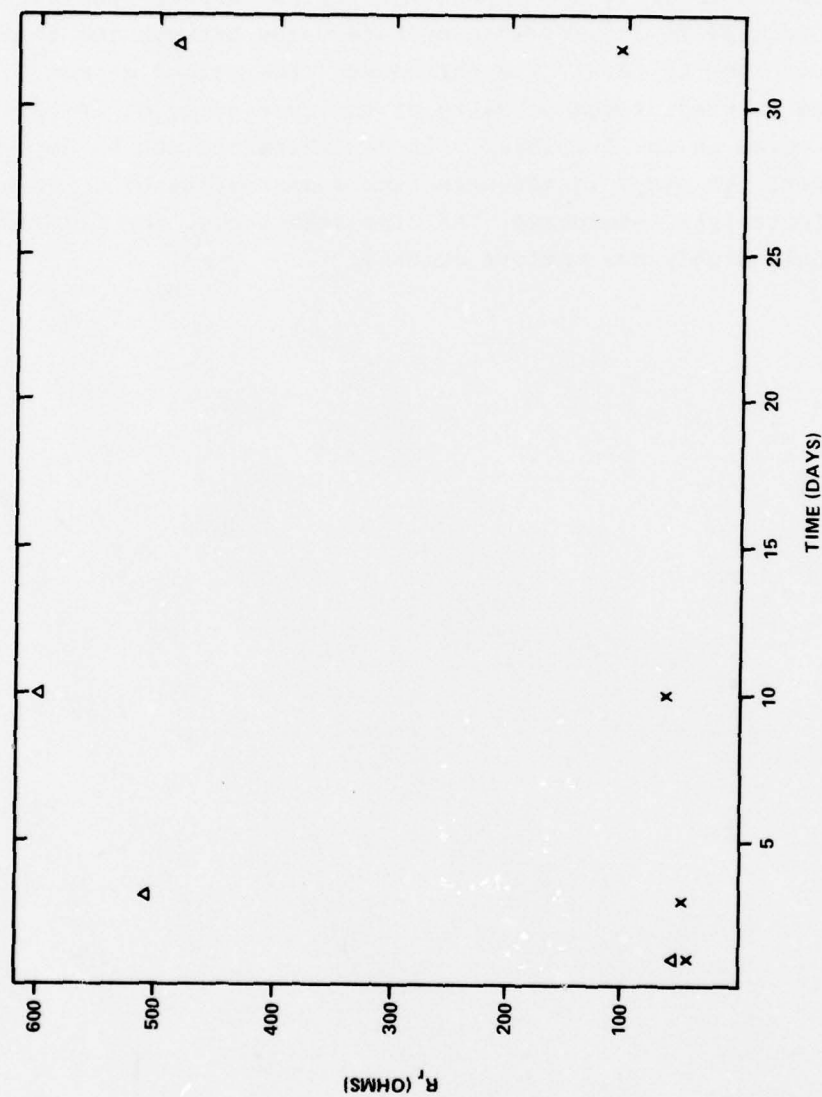


Figure 40. R_T For Representative Lithium Electrodes Immersed in .25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ Stored at Room Temperature (X) and 55°C (Δ).

resistivity as measured by pulse polarization techniques were much less in the boron electrolyte. The differences in the measured parameters cannot be explained by differences in electrolyte concentration, since Peled found less variation in d_{\min} and R_r by varying the concentration of LiAlCl_4 (18) than we have observed by changing the electrolyte salt. The measurement of the resistivity and capacitance by pulse polarization probably therefore results in some intermediate value between the thickness of the inner layer and the total film thickness. The method cannot be made to determine or predict the porosity of the overlayer, or the size or depth of the pores in the overlayer. It can therefore not be determined what role the overlayer plays in affecting the measurements of R_r or d_{\min} for the solid electrolyte interphase. As discussed above, the LiCl may consist of a single highly non-uniform coating.

3.4 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$: SEM OF LITHIUM SAMPLES AND COMPARISON WITH $\text{LiAlCl}_4/\text{SOCl}_2$

Even momentary exposure of lithium metal to electrolyte will result in the development of a film and chemical passivation. A piece of lithium immersed in 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$, then dried without rinsing produced Figures 41 and 42. After rinsing a sample with thionyl chloride to remove the electrolyte salt, the surface appeared as in Figures 43 and 44.

Scanning electron micrographs were taken of lithium samples stored for 19 days in 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$ at ambient temperature (Figures 45, 46, and 47) and at 55°C (Figures 48 and 49). For both samples, the lithium was found to be covered by a smooth passivating layer, with cubic crystals scattered over the surface. The smooth areas, much smoother than the original lithium, are believed to be a coating of salt, since the sample stored at room temperature developed cracks when flexed during mounting (Figure 50). At the time these photographs were taken, the EDAX was inoperative, preventing examination of the film for the presence of chlorine or sulfur. A different technique such as ESCA will be required to determine whether such films contain lithium or boron. The sample stored at 55°C had many more of the cubic crystals, interspersed with crystalline needles as shown in Figures 51 and 52. These needle-shaped crystals protruded from the surface as shown in the stereoscopic view in Figures 53R and 53L.

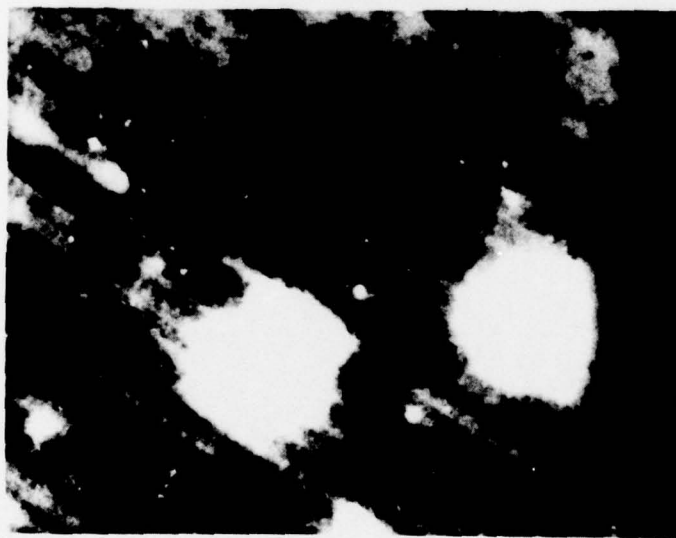


Figure 41. SEM of Lithium Surface Momentarily Dipped in 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$; X100.

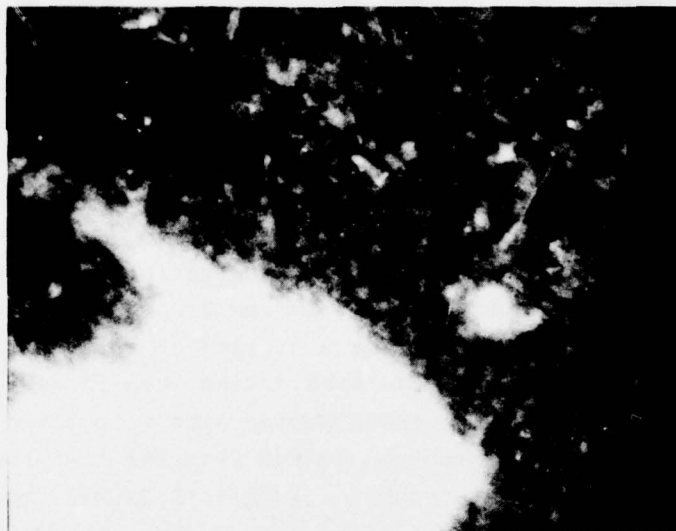


Figure 42. SEM of Lithium Surface Momentarily Dipped in 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$; X300.

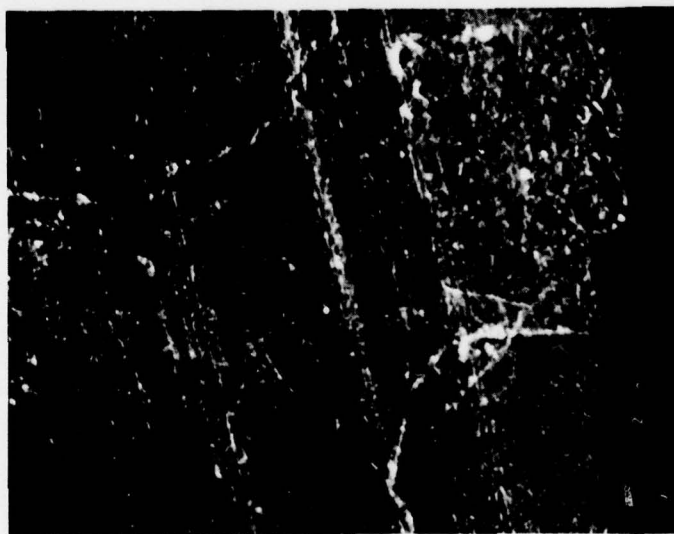


Figure 43. SEM of Lithium Surface Momentarily Dipped in 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$ and Rinsed with SOCl_2 ; X300.

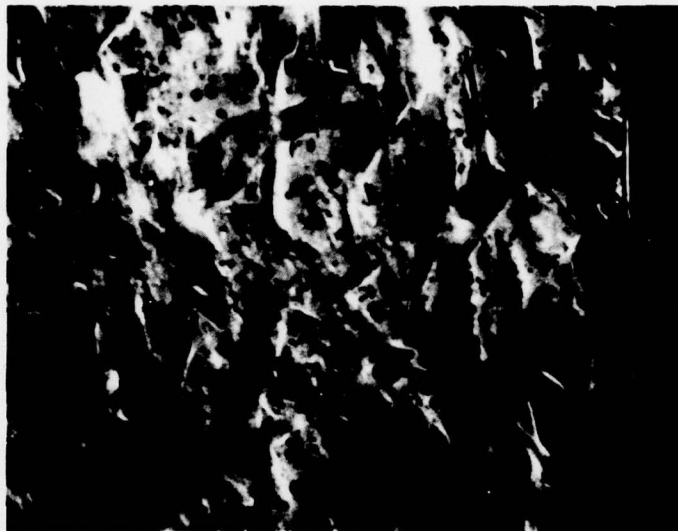


Figure 44. SEM of Lithium Surface Momentarily Dipped in 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$ and Rinsed with SOCl_2 ; X3000.

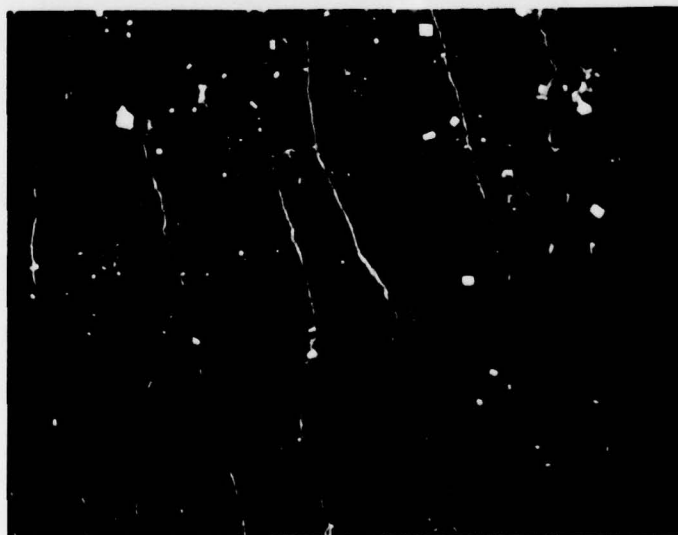


Figure 45. SEM of Lithium Surface Stored at Room Temperature for 19 Days in 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$; X1000.

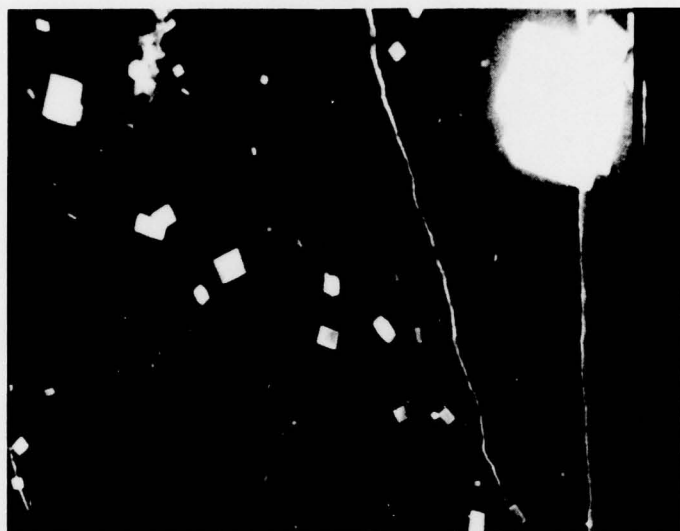


Figure 46. SEM of Lithium Surface Stored at Room Temperature for 19 Days in 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$; X3000.



Figure 47. SEM of Lithium Surface Exposed to 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$ for 19 Days at Room Temperature; X10,000.

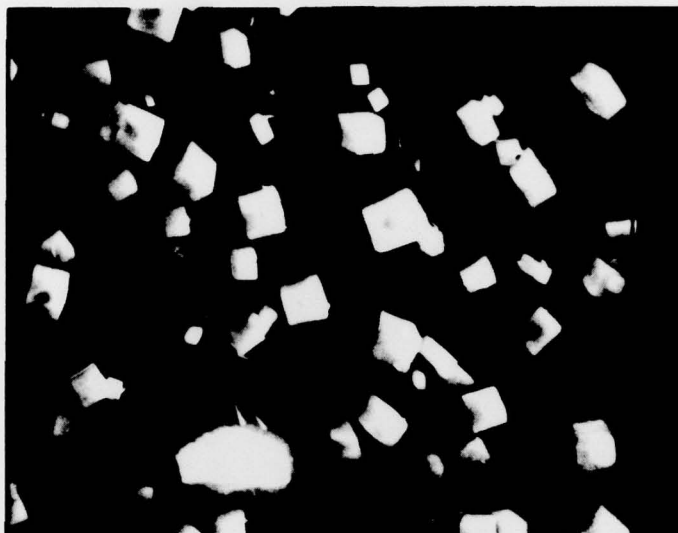


Figure 48. SEM of Lithium Surface Exposed to 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$ for 19 Days at 55°C; X1000.

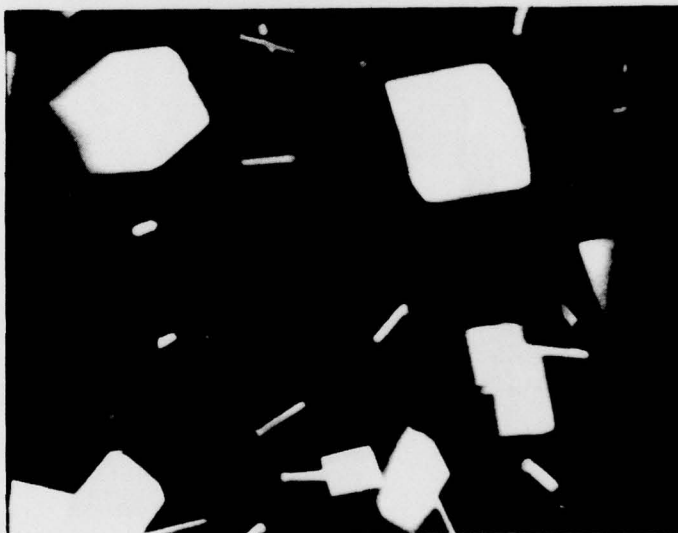


Figure 49. SEM of Lithium Surface Exposed to 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$ for 19 Days at 55°C; X3000.



Figure 50. SEM of Lithium Surface Exposed to 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$ for 19 Days at Room Temperature; X10,000.

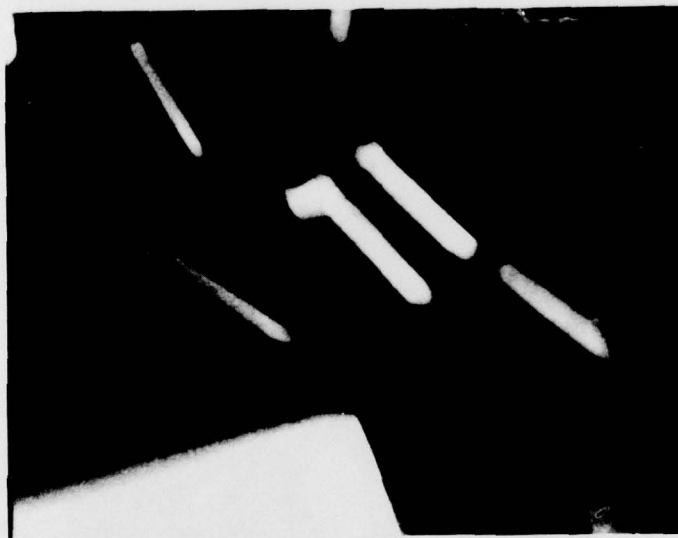


Figure 51. SEM of Lithium Exposed to 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$ for 19 Days at 55°C; X10,000



Figure 52. SEM of Lithium Surface Exposed to 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$ for 19 Days at 55°, X1000; 45° to normal

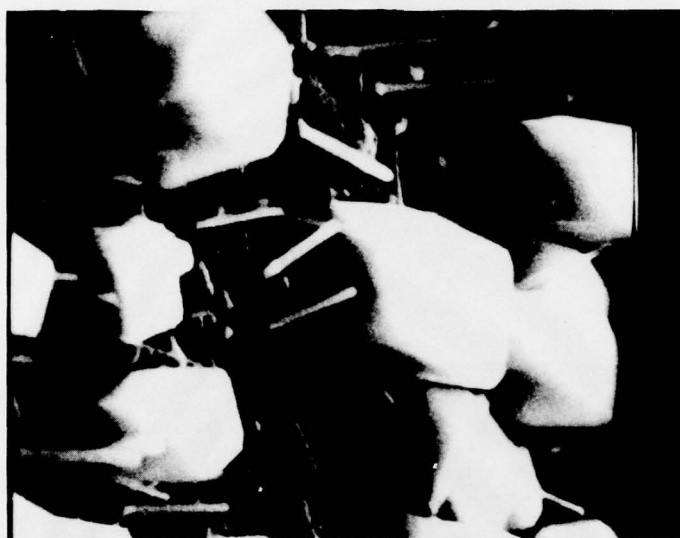


Figure 53. Stereoscopic View of Lithium Surface Exposed to 0.25 M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$ for 19 Days at 55°C; X3000, 45° to normal.

The cubic crystals might have been lithium chloride which had grown from species present in the solution as discussed above, rather than from simultaneous corrosion of lithium and solvent reduction. Lithium chloride is also known to grow from solutions of $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ in thionyl chloride (19). To explore this possibility, a piece of glass from the tube in which the lithium had been stored at 55° was also examined under the SEM. Cubic crystals could be seen on the monitor but they could not be photographed because of the charge which accumulated on the electrically insulating glass surface.

The extremely smooth chemically passivating surface on lithium stored in these solutions is remarkable and difficult to explain. The bright electropolishing or electrodeposition, or the chemical polishing of metals such as copper occur in aqueous solutions under the condition that the process has occurred randomly and non-crystallographically (20). This in turn occurs when copper transport is diffusion controlled. The random growth of a film of lithium chloride on lithium in $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$ might occur as the result of reaction at the surface of the metal without participation of dissolved lithium chloride near the interface. The surface also may lack crystallinity because it consists of a mixture of compounds rather than a single pure substance. It is possible that the smooth layer actually is the solid electrolyte interphase, essentially devoid of an overlayer. The appearance of the needle-shaped crystals is also distinctly different from the behavior of lithium surfaces exposed to $\text{LiAlCl}_4/\text{SOCl}_2$.

3.5 PHYSICAL PROPERTIES $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$: VISIBLE AND EPR SPECTRA

A visible spectrum of a dilute solution of $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ in SOCl_2 produced the result shown in Figure 54. While solutions of $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ in SOCl_2 appeared violet (15,19), both the salt and the solvent were colorless prior to the preparation of the solutions. Two absorptions were found, a prominent peak at 575 millimicrons and another less prominent one at 425 millimicrons. The spectrum shown in Figure 54 was taken shortly after mixing. The spectrum became more intense over a period of 4 days and then did not change any further. The formation of complexes and solvolysis reactions have been suggested to explain the color of these solutions, and the solid lithium chloride which crystallized on standing (19).

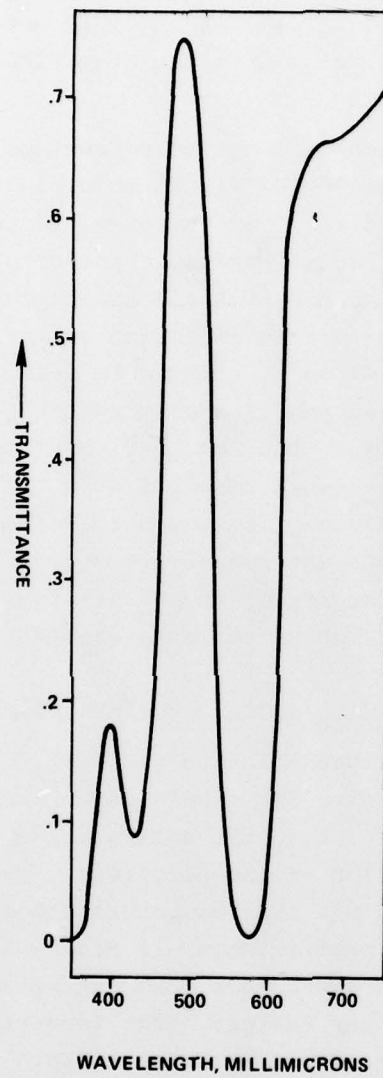


Figure 54. Visible Spectrum of $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$

The chemistry of $B_{10}Cl_{10}^{2-}$ has not been as extensively studied as that of its precursor, $B_{10}H_{10}^{2-}$. Blue colors have been associated with aqueous and non-aqueous oxidation of $B_{10}H_{10}^{2-}$ to a free radical with an absorption centered at about 550 millimicrons (21-23). The final products of the oxidation that forms this free radical appear to be partially halogenated boron cages, such as ions of the formula $B_{10}Cl_xB_{10-x}^{2-}$ (21). The anions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ also have been oxidized electrochemically, $B_{10}H_{10}^{2-}$ reversibly forming a free radical on oxidation. This radical can be easily reduced back to $B_{10}H_{10}^{2-}$ (24).

On the basis of the literature already mentioned, the violet color in $Li_2B_{10}Cl_{10}/SOCl_2$ might have been caused by the oxidation of the borate by thionyl chloride to produce a free radical. An electron paramagnetic resonance signal was indeed observed to develop over a period of 4 days following the dissolution of $Li_2B_{10}Cl_{10}$ in $SOCl_2$. The signal increased in the same time frame that the visible spectrum was observed to increase. the EPR g factor, or gyromagnetic ratio, was about 2 which is typical of many free radicals. The peak to peak width of the signal was about 640 gauss, which is unusual. We have no explanation for the large width of the signal. Since boron is about 20% B^{10} and 80% B^{11} and there are ten atoms in each polyhedral borate moiety, the number of lines expected from hyperfine splitting would be very large. No hyperfine splittings were observed. The free radical may be in a molecular orbital with about 20 - 30% atomic S orbital involvement. The strength of the signal indicated that it did not arise from an impurity or a minor reaction product.

The EPR signal was unaffected by whether the solution of $Li_2B_{10}Cl_{10}$ in $SOCl_2$ was made in air or vacuum or whether lithium was present. Upon evaporation, a signal was observed in the dark solid residue left behind. A sample of such residue when hydrolized was observed to give a violet color which persisted in solution for some hours. It was previously reported that $B_{10}Cl_{10}^{2-}$ can be recovered unchanged upon hydrolysis of $Li_2B_{10}Cl_{10}/SOCl_2$ (19). The resulting aqueous solution was colorless, but this could have resulted from the reduction of the radical in aqueous solution by the sulfur dioxide present as the product of hydrolysis of $SOCl_2$.

The violet color and the radical formation by $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ in SOCl_2 may be connected with the presence of the strongly polarizing lithium cation. For example, the bis-triethylammonium salt of $\text{B}_{10}\text{Cl}_{10}^{2-}$ when dissolved in SOCl_2 did not produce a violet colored solution (19). Similarly, the electrochemical oxidation of $\text{B}_{10}\text{H}_{10}^{2-}$ and its derivatives has been found to be affected by the cation present in solution. The potential of polarographic oxidation of $\text{B}_{10}\text{H}_8(\text{OH})_2^{2-}$ in aqueous solution was dependent upon the composition of the buffer solution used to vary the pH (25). These authors noted the inconsistency in their results but offered no explanation. The oxidation potential of $\text{B}_{10}\text{H}_{10}^{2-}$ in acetonitrile was reported to be +0.375 V vs. a standard calomel electrode in 0.1 M LiClO_4 , but +0.43 V in 0.1 M tetraethylammonium perchlorate (24).

The formation and presistence of a free radical in $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$ may be related to the "non-crystallographic" nature of the smooth passivating layer observed on lithium as described above, and ultimately to the mechanism by which $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ moderates the voltage delay problem. Solutions of lithium tetrachloroaluminate may differ from $\text{Li}_2\text{B}_{10}\text{Cl}_{10}/\text{SOCl}_2$ in having no stable free radical present in solution. The intermediate formed on discharge of Li/SOCl_2 cells could be a free radical such as $\cdot\text{SO}\cdot$ or $\text{SOCl}\cdot$, but the intermediate decomposes slowly even at ambient temperature to sulfur and sulfur dioxide (26). In the studies described in this report, the only discharge products present in solution were those present as the result of the direct reduction of the solvent by lithium metal. Introduction of materials capable of producing stable free radicals in $\text{LiAlCl}_4/\text{SOCl}_2$ may aid in reducing electrochemical passivation and voltage delay in Li/SOCl_2 cells.

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